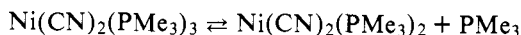


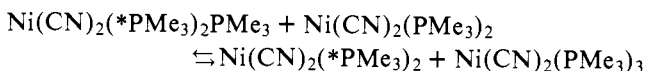
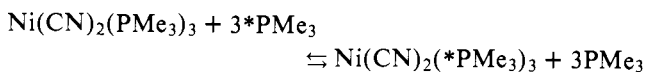
**Figure 1.**  $^{31}\text{P}\{^1\text{H}\}$  FT NMR spectra at 36.43 MHz of (a)  $\text{Ni}(\text{CN})_2(\text{PMe}_3)_2$ , 0.1 M, at  $-75^\circ\text{C}$ ; (b)  $\text{Ni}(\text{CN})_2(\text{PMe}_3)_3$ , 0.1 M, at  $-75^\circ\text{C}$ ; (c)  $\text{NiCl}_2(\text{PMe}_3)_3$ , 0.05 M, at  $-90^\circ\text{C}$  ( $J_{\text{PP}} = 78.8$  Hz); (d)  $\text{NiBr}_2(\text{PMe}_3)_3$ , 0.05 M, at  $-85^\circ\text{C}$  ( $J_{\text{PP}} = 70.3$  Hz); (e)  $\text{NiI}_2(\text{PMe}_3)_3$ , 0.05 M, at  $-75^\circ\text{C}$  ( $J_{\text{PP}} = 58.8$  Hz) in 1:1  $\text{CH}_2\text{Cl}_2\text{-CD}_2\text{Cl}_2$  solutions. The external reference is 65%  $\text{H}_3\text{PO}_4$  (not shown).

As the temperature is increased, intramolecular exchange occurs. Broadening of the lines and the collapse of the doublet and the triplet into a single line are observed and the rate constants increase in the order  $\text{I} < \text{Br} < \text{Cl}$ .

At  $-75^\circ\text{C}$ , the  $^{31}\text{P}$  NMR spectrum of  $\text{Ni}(\text{CN})_2(\text{PMe}_3)_3$  contains a weak singlet (<1%), characteristic of the trans square planar  $\text{Ni}(\text{CN})_2(\text{PMe}_3)_2$  species resulting from the dissociative process, although no free  $\text{PMe}_3$  is detected:

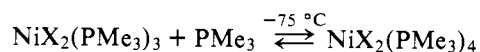


Addition of an excess of  $\text{PMe}_3$  to a  $\text{Ni}(\text{CN})_2(\text{PMe}_3)_3$  solution shows two singlets due to  $\text{Ni}(\text{CN})_2(\text{PMe}_3)_3$  and free  $\text{PMe}_3$ , at  $-75^\circ\text{C}$ . This complex provides an opportunity to investigate exchange of free and coordinated  $\text{PMe}_3$  at five-coordinate  $d^8$  metal centers. We have studied the following two reactions:



A line shape analysis, as a function of the concentration of the reactants at  $-20^\circ\text{C}$ , shows that these processes are first order in  $\text{Ni}(\text{CN})_2(\text{PMe}_3)_3$ , and zero order in  $\text{PMe}_3$  and  $\text{Ni}(\text{CN})_2(\text{PMe}_3)_2$ , respectively. The activation parameters are equal in both cases:  $\Delta H^* = +13.7 \pm 0.5$  kcal/mol and  $\Delta S^* = +10.4$  eu. For both reactions, we conclude a dissociative mechanism, with  $\text{Ni}(\text{CN})_2(\text{PMe}_3)_2$  acting as an intermediate.

When free  $\text{PMe}_3$  is added to the five-coordinate halide complexes, the quantitative formation of a new species occurs with the following stoichiometry:



The product is characterized by a singlet at  $\delta -14.9$  ppm for  $\text{X} = \text{Cl}$ ,  $\delta -15.8$  ppm for  $\text{X} = \text{Br}$ , and  $\delta -18.5$  ppm for  $\text{X} = \text{I}$ . When the molecular ratio  $\text{PMe}_3/\text{NiX}_2(\text{PMe}_3)_3$  is greater than one, the singlet due to free  $\text{PMe}_3$  appears at  $-61.2$  ppm. No other species is detected at this temperature.

An increase of the solution conductivity is observed when the temperature is lowered, indicating the presence of ionic species. For  $\text{X} = \text{Br}$ , the ligand field spectrum recorded under the same conditions of temperature and concentration contains only one symmetrical ligand field band, the  $\epsilon$  value ( $\sim 1900$ ) and energy ( $18\,400\text{ cm}^{-1}$ ) of which are characteristic of five-coordinate square pyramidal  $\text{Ni}(\text{II})$  complexes.<sup>9-11</sup> Thus, the presence of only one  $^{31}\text{P}$  NMR singlet and one nearly symmetrical ligand field transition favor the square pyramidal complex  $[\text{NiBr}(\text{PMe}_3)_4]\text{Br}$ , with the halide in the apical position. However, the recent report of the trigonal bipyramidal structure  $[\text{NiBr}(\text{P}(\text{OMe})_3)_4]\text{BF}_4$ <sup>12</sup> is not consistent with our conclusions.

The very few square pyramidal  $\text{Ni}(\text{II})$  complexes with monodentate tertiary phosphine ligands reported prompted us to continue structural studies along this line. Ligand exchange studies have also been initiated with a view to obtaining quantitative rate data. It is clear, from the results presented here, that  $^{31}\text{P}$  NMR is a useful technique for providing insight into the complicated chemistry of five-coordinate metal complexes containing monodentate phosphine ligands.

## References and Notes

- (1) P. Meakin and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 5751 (1974).
- (2) P. Meakin, R. A. Schunn, and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 277 (1974).
- (3) P. R. Hoffman and K. G. Caulton, *J. Am. Chem. Soc.*, **97**, 4221 (1975).
- (4) P. Rigo, C. Peale, and A. Turco, *Inorg. Chem.*, **6**, 1636 (1967).
- (5) C. G. Grimes and R. G. Pearson, *Inorg. Chem.*, **13**, 970 (1974).
- (6) D. A. Sweigart and P. Heldtmann, *J. Chem. Soc., Dalton Trans.*, 1686 (1975).
- (7) A. Merle, M. Dartiguenave, Y. Dartiguenave, I. W. Dawson, and H. B. Gray, *J. Coord. Chem.*, **3**, 199 (1974); I. W. Dawson, T. I. Bryant, N. R. Robinson, A. Merle, M. Dartiguenave, Y. Dartiguenave, and H. B. Gray, *J. Am. Chem. Soc.*, **96**, 4428 (1974).
- (8) L. M. Jackman and F. A. Cotton, "Dynamic Nuclear Resonance Spectroscopy", Academic Press, New York, N.Y., 1975, p 266.
- (9) C. Cloyd and D. W. Meek, *Inorg. Chim. Acta*, **6**, 4809 (1972).
- (10) C. A. MacAuliffe and D. W. Meek, *Inorg. Chem.*, **8**, 904 (1969).
- (11) J. R. Preer and H. B. Gray, *J. Am. Chem. Soc.*, **92**, 7306 (1970).
- (12) D. S. Millbrath, J. P. Springer, J. C. Clardy, and J. G. Verkade, *Inorg. Chem.*, **14**, 1665 (1975).

Pierre Meier, André E. Merbach

Institut de Chimie Minérale et Analytique  
Université de Lausanne  
CH-1005 Lausanne, Switzerland

Michèle Dartiguenave,\* Yves Dartiguenave

Laboratoire de Chimie de Coordination du CNRS, BP 4142  
31030 Toulouse, Cedex, France  
Received March 29, 1976

## Anion Cryptates: Highly Stable and Selective Macrotricyclic Anion Inclusion Complexes

Sir:

Whereas very many metal cation complexes are known, stable anion complexes of organic ligands are very rare indeed. Spherical cations (e.g., alkali cations) form very stable and selective cryptates where the cation is included in the intramolecular cavity of a macropolycyclic ligand.<sup>1</sup> Similarly, it should be possible to obtain stable and selective anion complexes, anion cryptates, by inclusion into cavities lined with appropriate anion binding sites, i.e., especially sites able to form ionic hydrogen bonds like protonated amines:  $\text{N}^+\text{-H}\cdots\text{X}^-$ .

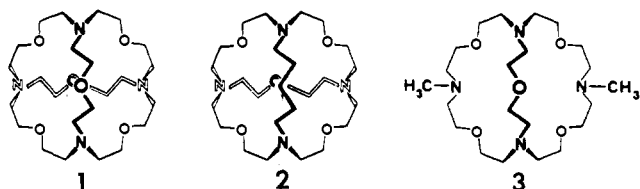
Indeed, halide ions give inclusion complexes, the katapinates,<sup>2</sup> in which the anion is held in the cavity of biprotonated macrobicyclic diamines  $^+\text{HN}[(\text{CH}_2)_n]_3\text{NH}^+$  by two hydrogen bonds,  $^+\text{N-H}\cdots\text{X}^-\cdots\text{H-N}^+$  as confirmed by a recent crystal structure determination.<sup>3</sup> Complexes of small anions with  $\alpha$ - and  $\beta$ -cyclodextrins have also been reported.<sup>4</sup>

**Table I.** Stability Constants, Log  $K_s$ , of the Anion Complexes of Ligands **1**, **2**, **3**, and **5**<sup>a</sup>

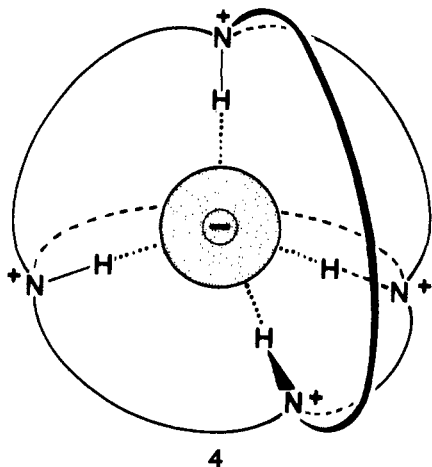
| Anion           | Solvent <sup>b</sup> | Log $K_s$ with ligand          |                                |                                |                                |
|-----------------|----------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
|                 |                      | 1-H <sub>4</sub> <sup>4+</sup> | 2-H <sub>4</sub> <sup>4+</sup> | 3-H <sub>4</sub> <sup>4+</sup> | 5-H <sub>2</sub> <sup>2+</sup> |
| Cl <sup>-</sup> | W                    | >4.0                           | >4.5                           | 1.7 ± 0.1                      | (~0.7) <sup>c,d</sup>          |
|                 | M/W                  | —                              | —                              | 3.1 ± 0.1                      | 2.1 ± 0.1                      |
| Br <sup>-</sup> | W                    | <1.0                           | 1.55 ± 0.1                     | <1.0                           | <1.0 <sup>d</sup>              |
|                 | M/W                  | 1.75 ± 0.2                     | 3.2 ± 0.1                      | 1.7 ± 0.2                      | ~1.2 ± 0.3                     |

<sup>a</sup> Stability constants determined using chloride and bromide ion selective electrode. For I<sup>-</sup>, log  $K_s$  < 1.0 in water; for the most stable chloride complexes (with **1** and **2**) only lower limits could be obtained because of insufficient sensitivity of the available electrodes. **5** = N[(CH<sub>2</sub>)<sub>10</sub>]<sub>3</sub>N, ref 2. <sup>b</sup> W: water at pH 1.50 (HNO<sub>3</sub>); M/W: methanol/water 9/1 at pH 1.30 (HNO<sub>3</sub>); temperature 22 °C. <sup>c</sup> Value estimated from the M/W result by comparison with the 3-H<sub>4</sub><sup>4+</sup> data. <sup>d</sup> Log  $K_s$  > 1.0 in 50% trifluoroacetic acid at 23 °C; see ref 2.

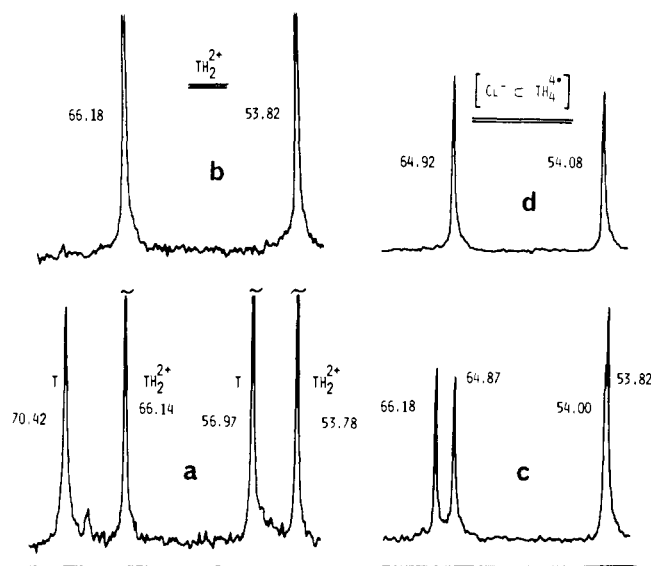
We have recently shown that the spheroidal ligand **1** forms cryptate complexes with various metal cations.<sup>5</sup> We now report that macrotricyclic ligands of this type also form remarkably stable and selective anion cryptates with the spherical halide anions. The synthesis of **1** has been reported;<sup>5</sup> its derivative **2** (mp 214–216 °C) has been obtained along the same lines; the macrobicyclic analogue **3** (oil) is prepared by Eschweiler-Clarke methylation of the corresponding bis-secondary amine (compound **10** in ref. 5).



Anion complexation may be observed by <sup>13</sup>C NMR spectroscopy. When methanolic HCl is added to a solution of **1** in methanol-*d*<sub>4</sub> the spectral changes shown in Figure 1 are obtained. With 1 equiv of HCl two species are present in about 1/1 ratio, the diprotonated tricycle TH<sub>2</sub><sup>2+</sup> and the free amine T perhaps in fast exchange with a small quantity TH<sup>+</sup>; at 2 equiv of HCl only TH<sub>2</sub><sup>2+</sup> is observed; with 3 equiv of HCl again two species are present in 1/1 ratio: TH<sub>2</sub><sup>2+</sup> and a new species **4**, into which the remaining TH<sub>2</sub><sup>2+</sup> is converted as more



acid is added. To identify **4**, the same experiment was performed using HNO<sub>3</sub> as acid. Up to 2 equiv of HNO<sub>3</sub> exactly the same species were observed as with HCl; above 2 equiv of HNO<sub>3</sub> the <sup>13</sup>C spectra are different from those obtained with HCl; however, when NMe<sub>4</sub><sup>+</sup>Cl<sup>-</sup> is added to the solution containing 4 equiv of HNO<sub>3</sub> (i.e., TH<sub>4</sub><sup>4+</sup>) a new species is obtained which is exactly the same as species **4** observed with 4 equiv of HCl (Figure 1). From this we deduce that this species **4** is the chloride inclusion complex [Cl<sup>-</sup> ⊂ TH<sub>4</sub><sup>4+</sup>] with T = **1**.



**Figure 1.** <sup>13</sup>C FT NMR spectra (25 MHz) of ligand **1** at increasing concentrations of HCl in methanol-*d*<sub>4</sub>: (a) 1 equiv, (b) 2 equiv, (c) 3 equiv, (d) 4 equiv of HCl. T: unprotonated ligand; TH<sub>2</sub><sup>2+</sup>: diprotonated **1**; shifts in parts per million from Me<sub>4</sub>Si.

Inclusion of F<sup>-</sup> and Br<sup>-</sup> in similar conditions is also observed by <sup>13</sup>C NMR. I<sup>-</sup> does not form a complex, nor do any of the polyatomic anions NO<sub>3</sub><sup>-</sup>, CF<sub>3</sub>COO<sup>-</sup>, or ClO<sub>4</sub><sup>-</sup>. The spectral results described also show that in the presence of Cl<sup>-</sup> the (1-H<sub>3</sub><sup>3+</sup>) species dismutates into (1-H<sub>2</sub><sup>2+</sup>) and [Cl<sup>-</sup> ⊂ 1-H<sub>4</sub><sup>4+</sup>], the tetraprotonated species being stabilized by Cl<sup>-</sup> complexation.

The structure of these anion cryptates is expected to be as schematically presented on formula **4**; the anion is held inside the molecular cavity of the cryptand in its tetraprotonated i<sub>4</sub><sup>4+</sup> form by a tetrahedral array of <sup>+</sup>N-H...X<sup>-</sup> hydrogen bonds. This has been confirmed by the determination of the crystal structure of [Cl<sup>-</sup> ⊂ 1-H<sub>4</sub><sup>4+</sup>].<sup>6</sup> Such a tetrahedral environment of the chloride ion corresponds to that found in ammonium halides in the solid state.<sup>7</sup> One may consider the tetraprotonated i<sub>4</sub><sup>4+</sup> form of spheroidal cryptands like **1** as the topologically optimal receptor for spherical anions (e.g., the halide ions) of size compatible with the size of the molecular cavity.

As in the case of cation cryptates,<sup>2,8</sup> such three-dimensional binding with complete inclusion should produce stable and selective anion cryptates. The distance from N to cavity center is about 3.2 Å. From the <sup>+</sup>N-H...F<sup>-</sup> distance in NH<sub>4</sub>F (2.705 Å)<sup>9</sup> and the ionic radii of the anions, the <sup>+</sup>N...X<sup>-</sup> distances for X = Cl, Br, I are about 3.18, 3.33, and 3.57 Å, respectively. Thus F<sup>-</sup>, Cl<sup>-</sup>, and Br<sup>-</sup> may enter the cavity, but I<sup>-</sup> is too large.

The stability constants  $K_s$  of the chloride and bromide inclusion complexes of the tetraprotonated forms of compounds

1–3 have been determined and are listed in Table I.<sup>10</sup>

(1) The *high stability* of the chloride cryptates of 1-H<sub>4</sub><sup>4+</sup> and 2-H<sub>4</sub><sup>4+</sup> is remarkable indeed. The most stable of the reported chloride katapinates, the chloride complex of the diprotonated form of N[(CH<sub>2</sub>)<sub>10</sub>]<sub>3</sub>N<sup>2+</sup>, **5**, is at least three orders of magnitude less stable (Table I). Thus, the present chloride cryptates are by far the most stable anion complexes known to date.

(2) Compounds 1-H<sub>4</sub><sup>4+</sup> and 2-H<sub>4</sub><sup>4+</sup> also display *high Cl<sup>-</sup>/Br<sup>-</sup> selectivity* (>1000) whereas 3-H<sub>4</sub><sup>4+</sup> and 5-H<sub>2</sub><sup>2+</sup> are much less selective (Table I).

(3) The results clearly show the operation of a topological *macrotricyclic cryptate effect* on both the stability and the selectivity of the anion complexes. The much higher stability as well as the very high Cl<sup>-</sup>/Br<sup>-</sup> selectivity of the spheroidal macrotricyclic ligands **1**, **2** as compared to the macrobicyclic ligand **3**, may be ascribed to the presence of a *closed and rigid cavity*, a feature characteristic of a ligand having high dimensionality, high connectivity, and high cyclic order.<sup>1</sup> These large effects arise from a better holding of the <sup>+</sup>N–H binding sites, efficient hindrance to hydration of the <sup>+</sup>N–H sites, and resistance to deformation, rendering the cavity unable to adjust to changes in anion size.

The effect of further structural modifications and the synthesis of other types of molecules will provide strategies for the rational design of organic anion receptors and carriers. Such results should be of interest in biology as well as in chemistry in view of the active current research on anion binding and transport in biological membranes (e.g., in red blood cells).<sup>11</sup>

## References and Notes

- (1) J. M. Lehn, *Struct. Bonding (Berlin)*, **16**, 1 (1973).
- (2) C. H. Park and H. E. Simmons, *J. Am. Chem. Soc.*, **90**, 2431 (1968).
- (3) R. A. Bell, G. G. Christoph, F. R. Fronzeck, and R. E. Marsh, *Science*, **190**, 151 (1975).
- (4) J. F. Wojcik and R. P. Rohrbach, *J. Phys. Chem.*, **79**, 2251 (1975).
- (5) E. Graf and J. M. Lehn, *J. Am. Chem. Soc.*, **97**, 5022 (1975).
- (6) B. Metz, J. M. Rosalky, and R. Weiss, *J. Chem. Soc., Chem. Commun.*, 533 (1976).
- (7) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, N.Y., 1968.
- (8) J. M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc.*, **97**, 6700 (1975).
- (9) B. Morosin, *Acta Crystallogr., Sect. B*, **26**, 1635 (1970).
- (10) F<sup>-</sup> also forms stable complexes. Because of F<sub>2</sub>H<sup>-</sup> formation at low pH, determination of log K<sub>s</sub> requires more detailed data analysis.
- (11) See, for instance, M. K. Ho and G. Guidotti, *J. Biol. Chem.*, **250**, 675 (1975); A. Rothstein, Z. I. Cabantchik, and P. Knauf, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, **35**, 3 (1976); *Nature (London)*, **255**, 193 (1975).
- (12) ERA No. 265 of the CNRS.

Ernest Graf, Jean-Marie Lehn\*

Institut Le Bel, Université Louis Pasteur  
67000 Strasbourg, France<sup>12</sup>

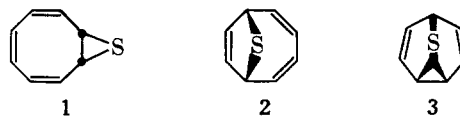
Received June 16, 1976

## Chemical Exploration of the C<sub>8</sub>H<sub>8</sub>S Energy Surface under Conditions of Mild Thermal Activation. Bond Relocations and Cycloadditions

Sir:

Prompted by active interest in the factors responsible for the development of heteroaromatic character<sup>1</sup> we recently gained multiple entry into the C<sub>8</sub>H<sub>8</sub>S system through isomers **1**,<sup>2</sup> **2**,<sup>2,3</sup> and **3**<sup>4</sup> and have since examined the pericyclic response of this well-characterized segment of the system to mild thermal activation (<100 °C) in an effort to (i) better understand the dynamics of isomerization among these systems and (ii) gain knowledge which might aid one in locating and, ultimately, isolating such coveted  $\pi$  transition and **4**, a heteroatomic analogue of the  $\pi$ -stabilized longicyclic carbanion.<sup>5</sup> In a previous publication on the subject we reported that mild

heating rapidly and irreversibly effects the conversion of **1** to **2** which (**2**), in turn, resists further change.<sup>2</sup> We now offer a deeper probe into the C<sub>8</sub>H<sub>8</sub>S energy surface with a description of thermal isomerizations originating from **3**.



As a heteroatomic analogue of the  $\pi$ -destabilized 9-barbaralyl anion,<sup>5</sup> sulfide **3** might be expected to be thermally labile and indeed it is. On warming to ambient temperature, it rapidly equilibrates into a two-component mixture of **4** (85%)<sup>6</sup> (white solid; <sup>1</sup>H NMR (100 MHz; CDCl<sub>3</sub>)  $\tau$  3.60–3.95 (4 H, sym-m, H<sub>6</sub> + H<sub>7</sub> + H<sub>8</sub> + H<sub>9</sub>), 4.17 (1 H, d, H<sub>4</sub>, J<sub>4,3</sub> = 11.0 Hz, J<sub>4,5</sub> = 8.0 Hz), 4.35 (1 H, dt, H<sub>3</sub>, J = 11.0 Hz, 2.0 Hz, 1.5 Hz), 6.50 (1 H, m, H<sub>1</sub>), 6.85 (1 H, m, H<sub>5</sub>); <sup>13</sup>C NMR (25 MHz; CDCl<sub>3</sub>; –31 °C) 31.67 ppm (1 C, C<sub>1</sub> or C<sub>5</sub>), 35.39 (1 C, C<sub>1</sub> or C<sub>5</sub>), 114.65 (1 C, C<sub>3</sub> or C<sub>4</sub>), 118.89 (1 C, C<sub>3</sub> or C<sub>4</sub>), 119.77 (2 C), 129.74 (2 C); m/e 136 (P<sup>+</sup>; 81%, 135 (100%)) and **3** (15%)<sup>6</sup> with k<sub>3</sub> → k<sub>4</sub> (34.6°) = (3.22 ± 0.15) × 10<sup>-4</sup> s<sup>-1</sup> ( $\Delta G^\ddagger$  = 22.9 kcal/mol)<sup>7</sup> and k<sub>4</sub> → k<sub>3</sub> (34.6°) = (9.33 ± 1.0) × 10<sup>-5</sup> s<sup>-1</sup> ( $\Delta G^\ddagger$  = 23.7 kcal/mol).<sup>7</sup> The structural assignment depicted in **4** draws primarily from the <sup>13</sup>C NMR spectrum which shows four of the molecule's six olefinic carbons, i.e., those associated with the isolated ethylenes, to occur in magnetically equivalent pairs. In turn, the mixture of **3** and **4** readily undergoes irreversible isomerization in boiling benzene to produce **5** (<sup>1</sup>H NMR (100 MHz; CDCl<sub>3</sub>)  $\tau$  3.60 (1 H, d, J = 6.5 Hz, 2.0 Hz), 3.9–4.3 (3 H, m), 4.4–4.6 (2 H, m), 5.24 (1 H, d, H<sub>a</sub>, J = 12.0 Hz, 4.0 Hz), 6.15 (1 H, bd, H<sub>b</sub>, J<sub>a,b</sub> = 12.0 Hz),  $\lambda_{\max}$  (CH<sub>3</sub>CN) 237 nm ( $\epsilon$  5000), 260 (2200); m/e 136 (P<sup>+</sup>; 83%), 135 (100%), in ca. 75% yield. Besides resting on fully consistent spectroscopic data, the structural assignment depicted in **5** receives added support from the ready conversion of this substance to benzothioephene (ir, NMR) on exposure to *o*-chloranil.

## Scheme 1

